Dependencies of Clathrate Hydrate Dissociation Fugacities on the Inverse Temperature and Inverse Pore Radius

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Presented are simple explicit relations for the equilibrium fugacity of single-component (single-guest) gas hydrates as a function of temperature. It is shown how relations of the form $\ln f = \alpha + \beta/T$ can be derived starting with a standard statistical-thermodynamic model based on the van der Waals−Platteeuw equation. In addition to this demonstration of the validity of empirical relations that have been previously presented in the literature for bulk hydrates, explicit relations of the form $\ln f = \alpha + \beta/T + \delta/rT$ (where r is the pore radius) are derived for hydrate formation in porous media. The validity of these explicit relations is established for both structure I and structure II hydrates involving hydrocarbons that have negligible water solubilities by comparison of predictions for bulk hydrates with experimental data. In addition to their ease of use, these relations explicitly show the role played by the standard model parameters in the prediction of hydrate equilibrium conditions.

Introduction

Gas hydrates are crystalline structures that belong to a group of solids known as clathrates and which involve a lattice made up of hydrogen-bonded water molecules that form cavities occupied by guest gas molecules. Gas hydrates form under low-temperature, high-pressure conditions, both above and below the freezing point of water. Under proper conditions, the lattice is stabilized by van der Waals forces through the occupation of specific cavities within the lattice by certain types of guest molecules. The type of guest molecule(s) present determines which of the three known crystal structures the lattice assumes.[1]

Based on experimental data (see, for example, refs 1−4), empirical relations for the equilibrium pressure of gas hydrates as a function of temperature have been presented in the literature for hydrate formation in the bulk. These empirical relations have not been shown to be derivable from the standard thermodynamic models that have been applied to predict hydrate formation, though the empirical relations show excellent correlations with the experimental data. In this work we present the derivation of the general form of these empirical relations for bulk hydrate formation starting with a standard statistical thermodynamic model and show how the physical model parameters affect the predicted equilibrium pressures.

Many of the hydrate deposits found in nature occur in permafrost regions or beneath deep oceans, where they are commonly found in sediment pores, acting as a cement holding the sediment together. Henry et al.[5] and Clarke et al.[6] have presented models, based on earlier statistical thermodynamic models (van der Waals and Platteeuw[7]), that allow the prediction of equilibrium pressures when the porous medium contains a single-size pore. In the approaches of Henry et al.[5] and Clarke et al.,[6] a term resulting from the capillary pressure is added to the equation of van der Waals and Platteeuw to interpret data[8] resulting from experiments with a porous medium having a broad pore-size distribution. In this work we present the derivation of a simple explicit relation for the equilibrium fugacity for hydrate formation in porous media starting from the full statistical-thermodynamic model.

Empirical Fits to Bulk Hydrate Data

Kamath[3] noted that the equilibrium pressures for hydrates with a single guest component are well fit by simple relations of the form

$$\ln(P_{eq}) = A + B/T \tag{1}$$

In eq 1 P_{eq} is the equilibrium pressure of the guest, T is the temperature, and A and B are fitted parameters. This simple form is similar to the Antoine-type equation[9] that can be used to predict vapor pressures and which is derived from the Clapeyron equation

$$\frac{d(\ln P_{vp})}{d(1/T)} = \frac{-\Delta H_v}{R\Delta Z_v} \tag{2}$$

where ΔH_v is the enthalpy of vaporization, P_{vp} is the vapor pressure, and ΔZ_v is the difference between the gas and liquid compressibility factors. Equation 2 reduces to

$$\ln(P_{vp}) = \left(\frac{-\Delta H_v}{R\Delta Z_v}\right)\frac{1}{T} + C$$

(where C is a constant), analogous to eq 1, if the ratio $\Delta H_v/\Delta Z_v$ is assumed to be constant. The approximation given by this equation for the vapor pressure of liquids has been found to give reasonable results for temperatures between the boiling and critical points of many

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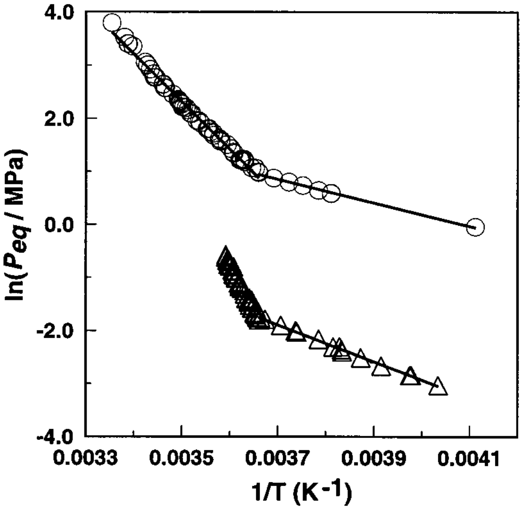

Figure 1. Experimental equilibrium pressures for methane (○) and propane (△) hydrates, as well as linear correlations using eq 1 and the parameters given in Table 1.

Table 1. Correlations for Fitting Experimental Equilibrium Pressures for Methane and Propane Hydrates to $\ln(P_{eq}) \approx A + B/T^a$

	A	B	temp range
methane	14.7170	−1886.79	248−273
	38.9803	−8533.8	273−298
propane	17.1560	−3269.6455	248−273
	67.1301	−16921.84	273−278

[a] P_{eq} is in kPa, and T is in K. Values are taken from work by Holder et al.[2]

substances.[9] Too much should not be inferred from the analogy between hydrate equilibrium pressures and vapor pressures suggested above. However, the apparent ability of equations of the form of eq 1 to fit experimental data for gas hydrates suggests that an equation of this form should be derivable from the statistical thermodynamic equations used to predict hydrate formation (just as eq 1 can be derived from eq 2). Figure 1 shows graphical representations of the correlations[2] (solid lines) given in Table 1 for methane and propane hydrates using eq 1. We note that while the correlations appear to be very good and have been noted by several authors (see, for example, refs 1, 2, and 4), no explanation based on the standard statistical thermodynamic model has been presented for their validity. Such an explanation is derived in the next section.

Modeling Hydrate Formation in the Bulk

Munck et al.[10] used a previously developed model[4] to obtain a single equation involving T_f and P_f (the temperature and pressure under which the hydrate forms) that can be used to predict hydrate formation conditions. In the case of hydrates formed from single-component gases, this equation takes the form

$$\frac{\Delta\mu_W{}^0}{RT_0} - \int_{T_0}^{T_f}\frac{\Delta H_W}{RT^2}\,dT + \int_0^{P_f}\frac{\Delta V_W}{R\bar{T}}\,dP - \ln(\gamma_W X_W) + \sum_i \eta_i \ln(1 - Y_i) = 0 \quad (3)$$

In eq 3, $\bar{T} = (T_0 + T_f)/2$, T_0 is the temperature of the standard reference state ($T = 273.15$ K and $P = 0$), $\Delta\mu_W{}^0$ is the chemical potential difference between the empty hydrate lattice and pure water in the reference state, η_i is the ratio of the number of cavities of type i to the number of water molecules in the hydrate lattice, and Y_i denotes the probability of a cavity of type i being occupied by the guest molecule. The probability Y_i is given in terms of the fugacity of the hydrate guest (f_i) in the gaseous state (calculated using the Soave−Redlich−Kwong equation of state) and the Langmuir adsorption constant (C_i) by

$$Y_i = \frac{C_i f}{1 + C_i f} \quad (4)$$

Additionally, $\Delta H_W = \Delta H_W{}^0 + \int_{T_0}^{T}\Delta C_p(T')\,dT'$, where $\Delta H_W{}^0$ is a reference enthalpy difference between the empty hydrate lattice and the pure water phase at the reference temperature, $\Delta C_p(T')$ is assumed to be constant[10] and equal to $\Delta C_p{}^0$ (the reference heat capacity difference), and ΔV_W is the volume difference between the empty hydrate and pure water (at T_0) and is assumed to be constant. Also note that the values used for $\Delta C_p{}^0$, $\Delta H_W{}^0$, and ΔV_W depend on whether the equilibrium involves liquid or solid water.

In this work, the temperature dependence of the Langmuir constants will be accounted for by using the form used by Munck et al.[10] and Parrish and Prausnitz[4]

$$C_i = (A_i/T)\exp(B_i/T) \quad (5)$$

where A_i and B_i are experimentally fit parameters and are dependent on which guest molecule is present, as well as which of the three hydrate structures is formed. The form of eq 5 results from the assumption of a square-well potential to model the interaction of the guest gas species with the surrounding water molecules.[11] Parrish and Prausnitz[4] used eq 5 for the Langmuir constants and reported a less than 0.2% error in using it relative to using the results of Lennard-Jones−Devonshire cell theory. The derivation that is presented below is independent of the assumed form of the Langmuir constants and only requires that their values be known at the temperature of interest. Below we present simple equations that can be used with any method of calculating the Langmuir constants, as well as ones based on using eq 5. The use of eq 5 to calculate the Langmuir constants has the advantageous characteristic of allowing us to investigate how the full statistical-thermodynamic model can be reduced to an explicit equation for the equilibrium gas fugacity that is similar in form to eq 1. In addition, the analysis described below could be applied to any of the various forms of eq 3 (all of which are based on the model presented by van der Waals and Platteeuw[7]) and not just to the form used by Munck et al.[10]

While eq 3 can be solved numerically for the equilibrium pressure by an iterative procedure (given any choice of temperature), it is not possible to solve for the pressure as a function of temperature, explicitly. Our goal is to find an accurate approximation of the true solution that allows such an explicit form to be determined.

We begin by a consideration of the terms involving either the pressure or fugacity of the gas. The first such term on the left-hand side of eq 3 involves the effect of the volume difference between the empty hydrate lattice and the normal state of the water, namely,

$$\int_0^{P_f}\frac{\Delta V_W}{R\bar{T}}\,dP = \frac{\Delta V_W}{R\bar{T}}P_f$$

Because of the relatively small volume change when hydrates form from water, the magnitude of this term is often small compared to others in eq 3. As a result of this, we consider $\ln f$ to be given by $f \approx \ln f^0 + \ln f^1$, where the second contribution (assumed small) is due to the $\Delta V_W/R\bar{T}P_f$ term in eq 3 and f^0 can be found by ignoring this term.

The other terms in eq 3 involving the pressure are those related to the cage occupancies

$$\sum_i \eta_i \ln(1 - Y_i) = \eta_s \ln(1 - Y_s) + \eta_l \ln(1 - Y_l) \quad (6)$$

where on the right-hand side we have used a subscript s to denote quantities for the "small" cages and l for those in "large" cages. Using the form for Y_i given in eq 4, each term of eq 6 can be rewritten using

$$\begin{aligned}\eta_i \ln(1 - Y_i) &= -\eta_i \ln(1 + C_i f)\\ &= -\eta_i \ln\left[C_i f\left(1 + \frac{1}{C_i f}\right)\right]\\ &= -\eta_i\left[\ln(C_i f) + \ln\left(1 + \frac{1}{C_i f}\right)\right] \quad (7)\end{aligned}$$

Clearly, if $C_i f$ is large enough, $\ln(1 + C_i f) \approx \ln(C_i f)$. If this approximation is not adequate (but $C_i f$ is still larger than unity), one can use a Taylor series expansion of the second logarithm in the last line of eq 5 to arrive at

$$\eta_i \ln(1 - Y_i) \approx -\eta_i\left[\ln(C_i f) + \frac{1}{C_i f} - \frac{1}{2}\left(\frac{1}{C_i f}\right)^2 + ...\right] \quad (8)$$

To demonstrate the validity of using $\ln(1 + C_i f) \approx \ln(C_i f)$, we shall consider its application to methane hydrates. The experimental temperatures and pressures found in work by Sloan,[1] as well as the second virial coefficient (used to convert these pressures to fugacities), have been used to construct Figure 2, where the percent errors in approximating $\ln(1 + C_i f)$ as $\ln(C_i f)$ for the small and large cages over the temperature range from 273.7 to 298.1 K are shown. Clearly, this approximation is extremely good for the large cages and has a maximum error of 5.5% for the small. Applying this approximation for both terms in eq 3 yields

$$\eta_s \ln(1 - Y_s) + \eta_l \ln(1 - Y_l) \approx (\eta_s + \eta_l) \ln f + \eta_s \ln C_s + \eta_l \ln C_l \quad (9)$$

The error resulting from using the approximations for both cages (as in eq 9) is also shown in Figure 2 for methane hydrates; it is less than 1.6%. For gases that can only occupy the large cages (such as propane), one only retains the term in eq 9 involving the large cages, and the approximation becomes $\eta_l \ln(1 - Y_l) \approx \eta_l \ln f + \eta_l \ln C_l$. Because this is equivalent to setting η_s equal

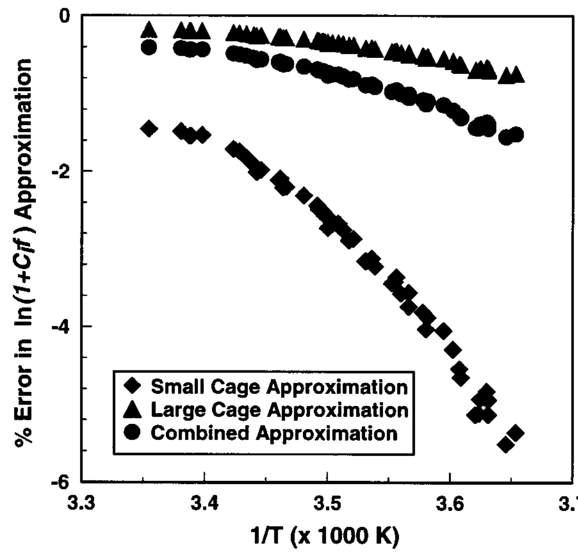

Figure 2. Percent errors in approximating $\ln(1 + C_i f)$ as $\ln(C_i f)$ for the large (▲) or small (◆) cages in methane hydrates, as well as the error (●) in using these approximations to compute the sum of the terms as appears in eq 9.

to zero in eq 9, the general equations presented below can also be used for the case when only the large cages are occupied by setting $\eta_s = 0$.

Using eq 9 in eq 3 and solving for $\ln f$ leads to

$$\begin{aligned}\ln f &\approx \frac{1}{\eta_s + \eta_l}\left[\frac{\Delta\mu_W^{\ 0}}{RT_0} - \int_{T_0}^{T_f}\frac{\Delta H_W}{RT^2}\,dT + \int_0^{P_f}\frac{\Delta V_W}{R\bar{T}}\,dP - \eta_s \ln C_s - \eta_l \ln C_l - \ln(\gamma_W X_W)\right]\\ &\approx \frac{1}{\eta_s + \eta_l}\left[\frac{\Delta\mu_W^{\ 0}}{RT_0} + \left(\frac{\Delta H_W^{\ 0} - T_0\Delta C_p^{\ 0}}{R}\right)\left(\frac{1}{T_f} - \frac{1}{T_0}\right) - \frac{\Delta C_p^{\ 0}}{R}\ln\left(\frac{T_f}{T_0}\right) + \frac{\Delta V_W}{R\bar{T}}P_f - \eta_s \ln C_s - \eta_l \ln C_l - \ln(\gamma_W X_W)\right] \quad (10)\end{aligned}$$

The second equality in eq 10 follows from carrying out the indicated integrations. For hydrocarbons such as methane and propane (where the gas solubility in water is very small), the last term on the right-hand side of eq 10 can be neglected.[10] As mentioned above, we compute $\ln f$ as $\ln f \approx f^0 + \ln f^1$, where the second term is small compared to the first and is due to the affect of the term involving P_f on the right-hand side of eq 10. For gas hydrates such as those involving methane or propane, the zeroth-order term of $\ln f$ is given by

$$\ln f^0 \approx \frac{1}{\eta_s + \eta_l}\left[\frac{\Delta\mu_W^{\ 0}}{RT_0} + \left(\frac{\Delta H_W^{\ 0} - T_0\Delta C_p^{\ 0}}{R}\right)\left(\frac{1}{T_f} - \frac{1}{T_0}\right) + \frac{\Delta C_p^{\ 0}}{R}\ln\left(\frac{T_0}{T_f}\right) - \eta_s \ln C_s - \eta_l \ln C_l\right] \quad (11)$$

Equation 11 can be used with any method for calculating the Langmuir constants (C_s and C_l). Using the form for the Langmuir constants given in eq 5 and using the identity $A_i/T = (A_i/T_0)(T_0/T)$ leads to

$$\ln f^0 \approx \frac{1}{\eta_s + \eta_l}\left[\frac{\Delta\mu_W^{\ 0} - \Delta H_W^{\ 0} + T_0 \Delta C_p^{\ 0}}{RT_0} - \eta_s \ln(A_s/T_0) - \eta_l \ln(A_l/T_0)\right] + \left[\frac{\Delta H_W^{\ 0} - T_0 \Delta C_p^{\ 0}}{R} - \eta_s(T_0 + B_s) - \eta_l(T_0 + B_l)\right]\frac{1}{T_f} + \left(\frac{\Delta C_p^{\ 0}}{R} - \eta_s - \eta_l\right)\ln\left(\frac{T_0}{T_f}\right) \approx a + b/T_f + c\ln(T_0/T_f) \tag{12}$$

The form of eq 12 is similar to the empirical equation ($\ln P_{eq} = A + B/T + C \ln T$) used by Parrish and Prausnitz[4] to describe the equilibrium pressures of several gas hydrates. If we now expand the logarithm involving T_0/T_f on the right-hand side of eq 12 about unity in terms of a power series in T_f/T_0 and truncate after the first nonzero term, we arrive at

$$\ln f^0 \approx \frac{1}{\eta_s + \eta_l}\left\{\frac{\Delta\mu_W^{\ 0} - \Delta H_W^{\ 0}}{RT_0} - \eta_s[\ln(A_s/T_0) - 1] - \eta_l[\ln(A_l/T_0) - 1]\right\} + \left[\frac{\Delta H_W^{\ 0}}{R} - \eta_s(T_0 + B_s) - \eta_l(T_0 + B_l)\right]\frac{1}{T_f} \approx \alpha + \beta/T_f \tag{13}$$

The expansion of $\ln(T_f/T_0)$ in powers of T_f/T_0 is done only to show how the relation given in eq 1 comes about and is not necessary to allow for the derivation of an explicit relation for the equilibrium guest fugacity. Clearly, the approximation represented by eq 13 will have an added error as compared to eq 12 when the difference between $(\Delta C_p^{\ 0}/R - \eta_s - \eta_l)\ln(T_0/T_f)$ and $(\Delta C_p^{\ 0}/R - \eta_s - \eta_l)(T_0/T_f - 1)$ becomes appreciable compared to the other terms on the right-hand side of eq 12.

Figure 3 shows predictions using eq 13 (with the parameter values given in Table 2) for methane hydrate (dotted trace), as well as the experimental data from ref 1 (pp 314−319) for hydrate equilibria involving liquid water. Even without including the correction for the volume change on hydrate formation, the maximum error is less than 4%. The correction term that must be applied can be estimated by assuming that the pressure in $\Delta V_W/R\bar{T}P_f$ can be approximated by f^0. Because the overall magnitude of this term is less than 4% of the remaining terms, the error in approximating P_f by f^0 will be very small. Therefore, using f^0 in place of P_f in eq 10 leads to

$$\ln f \approx \ln f^0 + \frac{\Delta V}{(\eta_s + \eta_l)R\bar{T}}\exp(\ln f^0) \tag{14}$$

with $\ln f^0$ given by either eq 12 or eq 13, depending on whether the approximation of $(\Delta C_p^{\ 0}/R - \eta_s - \eta_l)\ln(T_0/T_f)$ by $(\Delta C_p^{\ 0}/R - \eta_s - \eta_l)(T_0/T_f - 1)$ is allowable. Equation 14 is shown graphically in Figure 3 as the solid trace, where we have used eq 13 for $\ln f^0$. This approximation has a maximum error on the order of 1% over the temperature range from 273 to 298 K. As can be seen from the difference between the results of using eqs 13 and 14 in Figure 3, the second term on the right-hand side of eq 13 essentially results in a change in the slope of ln *f*. Unfortunately, because this term is not truly linear in $1/T$ but only appears so on the scale of ln *f*, the dominant part of this correction cannot be obtained from a Taylor series expansion about the point $1/T_0$. It can, however, be approximated by a straight line with only a small error (less than 0.5%), accounting for the high-quality fit that can be attained using a relation of the form of eq 1.

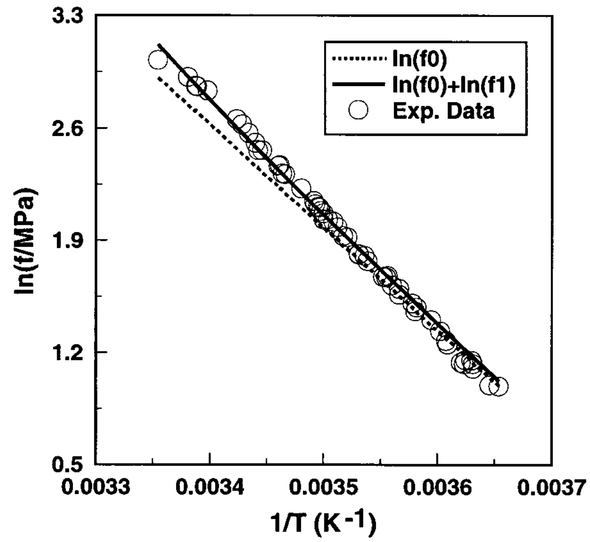

Figure 3. Experimental data (○) for methane hydrate formation, as well as approximations using eq 13 (···) and eq 14 (—).

Table 2. Parameter Values for Hydrate Formation[a]

property	unit	methane	propane
$\Delta\mu_W^0$	J/mol	1264	883
$(\Delta H_W^0)_{liq}$	J/mol	−4858	−5201
$(\Delta H_W^0)_{sol}$	J/mol	1151	808
$(\Delta C_p^0)_{liq}$	J/mol·K	39.16	39.16
$(\Delta C_p^0)_{sol}$	J/mol·K	0.0	0.0
$(\Delta V_W)_{liq}$	cm³/mol	4.6	5.0
$(\Delta V_W)_{sol}$	cm³/mol	3.0	3.4
σ_{hW}	J/m²	0.0267[b]	0.0267[b]
A_i	K/atm	0.0007228 (small cavity)	0.0 (small cavity)
		0.02335 (large cavity)	0.005455 (large cavity)
B_i	K	3187 (small cavity)	0.0 (small cavity)
		2653 (large cavity)	4638 (large cavity)

[a] All values are taken from Munck et al.,[10] except where noted. [b] From Clennell et al.[13]

Equation 14 can also be used for hydrate equilibria involving ice, except that different values of ΔC_p^0, ΔH_W^0, and ΔV_W (see Table 2) must be used. Plots of fugacities for methane hydrate equilibria involving liquid water as well as those involving ice are shown in Figure 4, along with the corresponding experimental data from ref 1 (pp 324−327).

As mentioned above, large gas molecules such as propane can enter only the large cages of a hydrate structure. As a result, eq 14 cannot be used directly, because in the derivation of eq 14 it was assumed that both cages were occupied at reasonably high levels. However, if the same derivation as that described above is performed after eliminating the term for the small cages in eq 9 by setting $Y_s = 0$, the result is exactly the same as using eq 14 with $\eta_s = 0$. Therefore, eq 14 can be used for hydrates that involve gases that can only enter the large cages as long as the substitution $\eta_s = 0$ is used. The results of applying eq 14 to propane (which

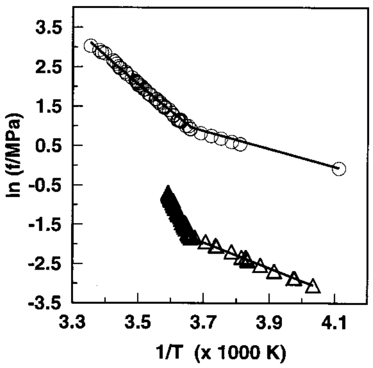

Figure 4. Experimental equilibrium fugacities for methane (○) and propane (△) hydrates, as well as predictions using eq 14 and the parameters given in Table 2.

forms structure II hydrates) are shown in Figure 4, again using eq 13 for ln f^0. Because the formation pressure for propane hydrate is lower than that for methane, one might expect the validity of the approximation in eq 9 to be decreased. However, because propane can only occupy the large cages in the hydrate and because these are occupied to a large extent at the temperatures considered here, the approximation is, in fact, more valid than it is for methane. For example, the maximum error in using the approximation in eq 9 for propane is less than 0.2% when the term $\eta_l \ln(1 - Y_l)$ is replaced by $\eta_l \ln f + \eta_l \ln C_l$.

An equation similar to eq 14 can also be derived for hydrates of gases such as CO_2 that have appreciable solubilities.[12]

Modeling Hydrate Formation in Porous Media

To describe hydrate formation in porous media, eq 3 must be modified to include the effect of the relevant interface on the activity of the water. After the necessary modifications are made in the region where the equilibria involve liquid water, eq 3 becomes[5]

$$\frac{\Delta\mu_W{}^0}{RT_0} - \int_{T_0}^{T_f}\frac{\Delta H_W}{RT^2}\,dT + \int_0^{P_f}\frac{\Delta V_W}{R\bar{T}}\,dP - \ln(\gamma_W X_W) + \sum_i \eta_i \ln(1 - Y_i) + V_L\frac{2\cos(\theta)\sigma}{RT_f r} = 0 \quad (15)$$

We note that Clarke et al.[6] presented a similar equation based on the assumption of a different interface. In eq 15, V_L is the molar volume of water in the aqueous phase, θ is the contact angle between the aqueous phase and the hydrate, σ is the surface tension of the relevant interface involving the hydrate phase, and r is the radius of a pore in the porous medium. Because the solubility of most guests in water is small, these parameters are approximated by their values for pure water. Equation 15 can be used for all temperatures, though some of the parameters will have different values depending on whether the temperature is above or below the ice point of water in the corresponding pore of radius r. Below this temperature one recovers the same equation as that given above for the bulk because the current model assumes that there are no surface effects between ice and hydrate. For hydrates such as those being considered in this work (where the water solubility of the gas is negligible), the melting temperature of ice in a pore of radius r can be found from[13]

$$T_m^{\text{pore}} = T_m^{\text{bulk}}\left(1 - \frac{2\sigma_{iW}}{\rho_W \Delta H_{fW} r}\right) \quad (16)$$

In eq 16, T_m^{bulk} is the bulk melting temperature (273.15 K), σ_{iW} is the surface tension between water and ice (0.0267 J/m^2), ρ_W is the specific density of water (1000 kg/m^3), and ΔH_{fW} is the specific enthalpy of fusion of bulk water (333 kJ/kg).

Performing the same analysis on eq 15 as that described above for eq 3, we arrive at (for methane and other hydrates where gas solubility is negligible)

$$\ln f_{\text{pore}}{}^0 \approx \frac{1}{\eta_s + \eta_l}\left[\frac{\Delta\mu_W{}^0}{RT_0} + \left(\frac{\Delta H_W{}^0 - T_0\Delta C_p{}^0}{R}\right)\left(\frac{1}{T_f} - \frac{1}{T_0}\right) + \frac{\Delta C_p{}^0}{R}\ln\left(\frac{T_0}{T_f}\right) - \eta_s \ln C_s - \eta_l \ln C_l + \left(\frac{2V_L\cos(\theta)\sigma}{R}\right)\frac{1}{T_f r}\right] \quad (17)$$

Using the form of C_i given by eq 5 yields

$$\ln f_{\text{pore}}{}^0 \approx \frac{1}{\eta_s + \eta_l}\left\{\left(\frac{\Delta\mu_W{}^0 - \Delta H_W{}^0 + T_0\Delta C_p{}^0}{RT_0} - \eta_s[\ln(A_s/T_0)] - \eta_l[\ln(A_l/T_0)]\right) + \left[\frac{\Delta H_W{}^0 - T_0\Delta C_p{}^0}{R} - \eta_s(T_0 + B_s) - \eta_l(T_0 + B_l)\right]\frac{1}{T_f} + \left(\frac{\Delta C_p{}^0}{R} - \eta_s - \eta_l\right)\ln(T_0/T_f) + \left(\frac{2V_L\cos(\theta)\sigma}{R}\right)\frac{1}{T_f r}\right\} \approx a + b/T_f + c\ln(T_0/T_f) + d/T_f r \quad (18)$$

If we again approximate $\ln(T_0/T_f)$ as $T_0/T_f - 1$, then for temperatures reasonably close to T_0 we arrive at

$$\ln f_{\text{pore}}{}^0 \approx \frac{1}{\eta_s + \eta_l}\left\{\left[\frac{\Delta\mu_W{}^0 - \Delta H_W{}^0}{RT_0} - \eta_s[\ln(A_s/T_0) - 1] - \eta_l[\ln(A_l/T_0) - 1]\right] + \left[\frac{\Delta H_W{}^0}{R} - \eta_s(T_0 + B_s) - \eta_l(T_0 + B_l)\right]\frac{1}{T_f} + \left(\frac{2V_L\cos(\theta)\sigma}{R}\right)\frac{1}{T_f r}\right\} \approx \alpha + \beta/T_f + \delta/T_f r \quad (19)$$

We note that *a, b, and c in eq 12 are identical to those in eq 18, as are the* α*'s and* β*'s in eqs 13 and 19*. Because at any given temperature the equilibrium fugacity in a porous medium should be higher than that in the bulk, the magnitude of $C_i f$ will be larger, making the approximations used in eq 9 to compute $\ln f_{\text{pore}}{}^0$ even more accurate in the porous medium. Computing the correction due to the volume change and calculating the total fugacity, we find (similar to eq 14)

$$\ln f_{\text{pore}} \approx \ln f_{\text{pore}}{}^0 + \frac{\Delta V}{(\eta_s + \eta_l)R\bar{T}}\exp(\ln f_{\text{pore}}{}^0) \quad (20)$$

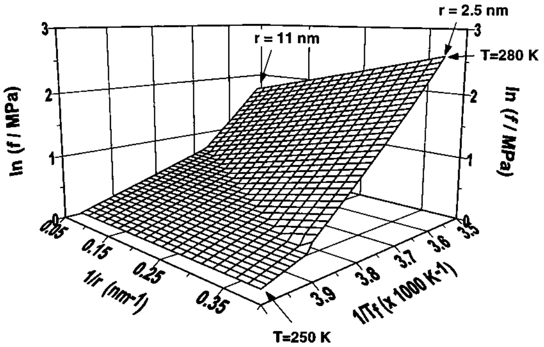

Figure 5. Surface representing predicted methane hydrate formation conditions in porous media using eq 20.

In eq 20, $\ln f_{\text{pore}}^0$ is given by either eq 18 or eq 19 depending on whether the approximation of $\ln(T_0/T_f)$ by $T_0/T_f - 1$ is allowable. For those cases where it is, eq 20 reduces to

$$\ln f_{\text{pore}} \approx \alpha + \frac{\beta}{T_f} + \frac{\delta}{T_f r} + \frac{\Delta V \exp(\alpha + \beta/T_f + \delta/T_f r)}{(\eta_s + \eta_l)R\bar{T}} \tag{21}$$

Because the last term in eq 21 should be a small correction, eq 19 suggests that the logarithm of the gas fugacity for simple hydrates in porous media should be very close to a bilinear function of $1/T$ and $1/r$. The form of eq 19 is called bilinear because for a fixed value of $1/T$ the function is linear in $1/r$, while for any fixed value of $1/r$, it is linear in $1/T$. The complete surface, however, does have a very small amount of curvature due to the overall nonlinearity of its functional form, though it is so small that it is difficult to see in Figure 5, where eq 20 has been used to generate the surface for methane hydrate formation in porous media for temperatures above T_m^{pore}. In generating this figure, we have used the value of 0.0267 J/m^2 for the surface tension between hydrate and liquid water proposed by Henry et al.[5] Other researchers have proposed different values for the surface tension which could also be used in eq 20. Consistent with the value of σ proposed by Henry et al.[5] is the assumption that the surface tension between hydrate and ice is negligible.[14,15] Under these conditions, eq 20 reduces to eq 14. Therefore, for temperatures below T_m^{pore}, eq 14 has been used to construct the portion of Figure 5 for hydrate equilibria involving ice. As noted above, the relations presented here are not dependent on the assumption of any specific value of the surface tension, and eq 20 could be applied to any choice of σ for the liquid water and/or ice regions. As can be seen in the figure, both regions appear to be nearly planar. We note that the average percent difference between the gas fugacities calculated with eq 20 using eq 19 for $\ln f_{\text{pore}}^0$ and those obtain using eq 18 for $\ln f_{\text{pore}}^0$ is 0.46% over the temperature and pore-size ranges depicted in Figure 5. In addition, the average error in using eq 20 with eq 18 for $\ln f_{\text{pore}}^0$ instead of the full model given by eq 3 is 3.3%. The corresponding figure for propane hydrate is shown in Figure 6. We note that this figure does not contain the same range of (r, T) points as Figure 5 because for some of the points in Figure 5 the pressure is large enough to liquefy the propane. For this structure II hydrate, the average error in calculating the gas fugacity using eq 21 with either eq 18 or eq 19 for $\ln f_{\text{pore}}^0$ is less than 1% (when compared to using eq 3) for the points shown in Figure

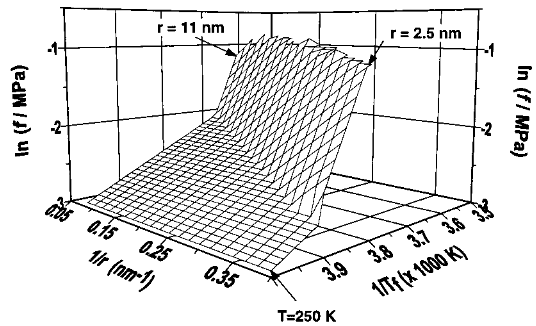

Figure 6. Surface representing predicted propane hydrate formation conditions in porous media using eq 20.

6. We note that, because of the smallness of the last term in eq 21, it can be approximated by a bilinear function. Therefore, under a broad range of conditions, it is possible to determine constants $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\delta}$ such that $\ln f_{\text{pore}} \approx \tilde{\alpha} + \tilde{\beta}/T_f + \tilde{\delta}/T_f r$, where $\tilde{\alpha}$, $\tilde{\beta}$, and $\tilde{\delta}$ are parameters that have values close to those given by eq 21.

Conclusions

In this work we have presented explicit relations for the equilibrium fugacities of gas hydrates with a single guest component under bulk conditions, as well as for hydrates in porous media. The validity of these relations has been demonstrated for both a structure I (methane) and a structure II (propane) hydrate. The relations derived here are approximations based on the more accurate statistical thermodynamic model commonly used to predict hydrate equilibrium conditions. By assuming a simple, tested, explicit form for the Langmuir constants, we demonstrated that the form of previously used empirical relations can be derived from the full statistical-thermodynamic model. Explicit relations are also presented that can be used along with other methods to calculate the Langmuir constants when the explicit form given in eq 5 may not be valid. The relations presented here are the first to explicitly show how equilibrium gas hydrate conditions depend on the standard model parameters. It has been demonstrated that, similar to the equation for bulk hydrates, a very simple equation of the form

$$\ln f_{\text{pore}} \approx \tilde{\alpha} + \tilde{\beta}/T_f + \tilde{\delta}/T_f r$$

should be able to be used to predict hydrate formation in porous media under a wide range of conditions.

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